PFPE, A Unique Lubricant for a Unique Application

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1998

Abstract: PFPE (Perfluoropolyether) is a clear colorless fluorinated synthetic oil that is nonreactive, nonflammable, safe in chemical and oxygen service, and is long lasting. PFPE grease is made by mixing different types of non-soap thickeners with the PFPE base oil. This paper highlights the unique properties (physical and chemical) of the PFPE as well as its unique application in areas where other lubricants are deficient. This paper includes methods of applying PFPE in oil and grease form, manufacturing of PFPE, and the benefits of using PFPE lubricants. Also, it includes a general overview of a hybrid grease--a grease suitable for less severe applications than PFPE yet superior to conventional greases produced by combining fluorinated greases with mineral/synthetic oils.

Key Words: Thermogravimetric analysis (TGA); Fourier transform infrared spectroscopy (FTIR); X-ray fluorescence (XRF); synthetic lubricant; lubricant degradation; lubricant properties; grease plating; vacuum impregnating, hybrid greases.

Introduction: PFPE, also called perfluoroalkylether (PFAE), or perfluoropolyalkylether (PFPAE), oils and oil-based greases are being used with an increasing frequency in spacecraft systems because of their favorable properties which include a wide application temperature range (see figure II), a good viscosity index, and general chemical inertness. The chemical inertness, however, must be evaluated in the light of extended satellite mission lifetimes and the rigors of operation in the orbital environment.

As with any other grease, PFPE grease consists of an oil, thickener, and in some cases additives. The base oil is the key component in the lubrication regime. The base oil is a polymer with a molecular weight range from 3000 to 13000 gm/gm mole, with viscosities varying from 2 cSt to 100 cSt at 100°C. The chemical structure of the base oil can be straight chain or branched chain (Z and Y fluids respectively) (see table I). The physical properties of the base oil depend on the structure of the polymeric chain. The thickener is usually Polytetrafluoroethylene (PTFE), or if the application requires a high thermally stable grease various types of fumed silica can be used.

CHEMICAL STRUCTURE OF PFPE

HYDROFLUOROETHYLENE : $F\text{-}(\text{-}CF(CF_3)\text{-}CF_2\text{-}O\text{-})_n\text{-}CF_2\text{-}CF_3$
(HEPO)

$n = 10\text{-}60$

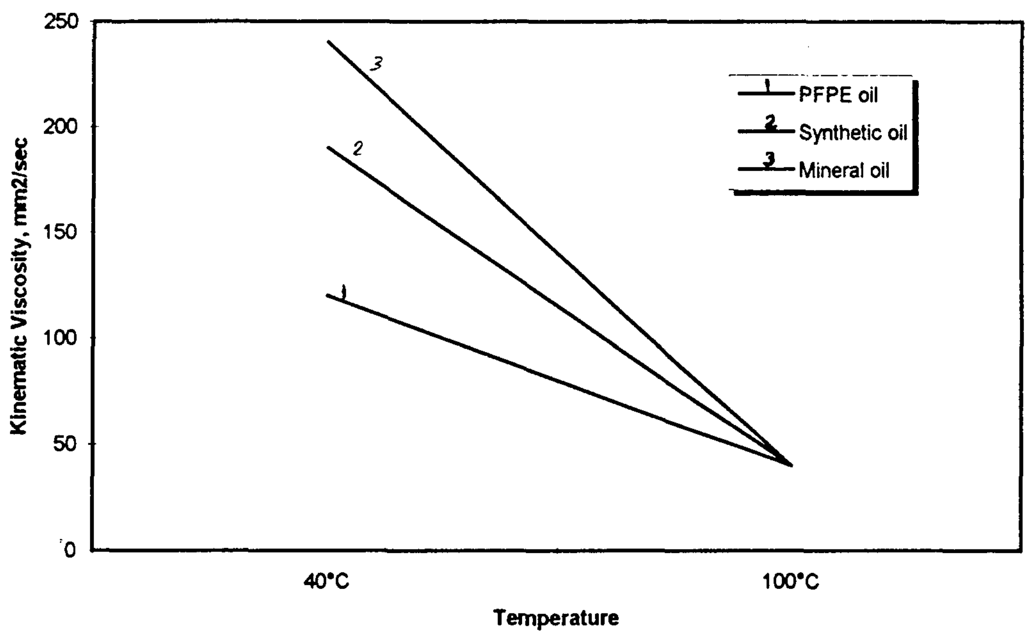
TETRAFLUOROETHYLENE : $CF_3\text{-}(\text{-}O\text{-}CF_2\text{-}CF_2\text{-})_p\text{-}(\text{-}O\text{-}CF_2)_q\text{-}OCF_3$
(TFE)

$p/q < 0.8$

PERFLUOROTRIMETHYLENEOXIDE : $F\text{-}(\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}O\text{-})_n\text{-}CF_2\text{-}CF_3$
(PFTMO)

$n = 10 - 60$

Table (I)



Viscosity-temperature slope (ASTM) as a function of kinematic Viscosity at 40°C and 100°C for different oils.

Figure I

BENEFITS OF PFPE LUBRICANTS

Bearing cleanliness: It is important to select the proper PFPE for the specific application. Both PFPE oil and grease lubricants provide a viscous, hydrodynamic film sufficient to support the load and separate ball from the raceway in bearing applications. Usually greases are displaced during the initial run in and remain fixed in place during their life. The oil in the thickener will bleed into the raceway. In high speed bearings, the oil is agitated severely producing an oil mist. This also occurs in slow speed bearings but to a lesser extent. This oil mist can migrate outside the bearing cavity. Therefore, it is preferable to use an inert oil, like one of the PFPE oils.

Excellent outgassing : PFPE is the best lubricant for the clean room, in the electronics industry because of it's very low outgassing properties compared to any other lubricants, and it does not outgas any hydrocarbons. Hydrocarbons will outgas low molecular weight hydrocarbons which will react with other materials. Ester based lubricants also react similarly to hydrocarbons. Synthetic hydrocarbons will outgass less than mineral based lubricant but still can be considered reactive. Silicone lubricants have a strong desire to migrate and may adversely affect electrical conductivity of electrical contacts.

Low pour point and vapor pressure : PFPE, Z type, has a straight chain molecular structure which enables it to flow freely at very low temperature, (freezing point < -100°F). Also, it has a low vapor pressure at 20°C = < 4 x 10^{-13} torr. These two properties are the two most important properties for space application

Fire resistant: The PFPE oils and greases are not combustible under any circumstances making PFPEs safe to use in various critical applications, where fire resistance is a requirement.

Low surface tension: Low surface tension, 20 dyn/cm at 20°C, will ensure that oil will reach the narrow gaps in any machine it lubricates and also gives the highest oil to surface affinity, (see table II).

High Viscosity Index: A wide range of Kinematic Viscosity fluids with a high Viscosity Index, VI = 350, makes certain PFPE oils most suitable for applications that requires a small change in viscosity over a wide range of temperature (see Figure I).

Extreme Pressure: In the ASTM D-2596, 4-ball Weld Point Test, unadditised PFPE provides a pass result above 800kg. This property makes the PFPE a good lubricant in any application where a requirement exists for extreme pressure properties.

Safe operation: General chemical inertness and radiation resistance of the PFPE makes it the lubricant of choice in chemical and nuclear facilities.

Nontoxic and biologically inert: PFPE oil and grease applications are the safest among any other lubricant application. PFPE's relative non-toxicity and biological inertness makes it a preferred lubricant in the food and pharmaceutical industries.

Comparative Temperature Limits

Degrees Fahrenheit

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|____|____|____|____|____|____|____|____|____|____|____|____|____|
-120 -100 -80  -60  -40  -20   0    20   200  300  400  500  600  700

                  <---------- Mineral Oil ------------>

             <-------------------- Polyglycol ---------------------->

          <--------------- Synthetic Hydrocarbon ------------------>

        <---------------------- Dibasic Acid Ester ----------------------->

      <------------------------- Polyol Ester ------------------------------->

<------------------------------------- Perfluoropolyether ----------------------------->
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Figure (II)

Comparative Surface tensions

Liquid in contact with air	Surface tension at 20°C dyne/cm
Perfluoropolyether	18 - 24
Ethyl Alcohol	22
Polyalphaolefin	25 - 29
Mineral oil	34
Water	73
Mercury	465

Table (II)

OTHER BENEFITS OF PFPE

- Wide temperature range.
- Low oil separation & outgassing/volatility.
- Long shelf life and storage stability.
- High oil VI and low pour point.
- High oxidative and thermal stability.

PFPE TYPICAL APPLICATIONS

- Aircraft instrument bearing grease.
- Air conditioning bearing and cabin pressurization valves on aircraft.
- Moderate to high radiation resistant lubricant applications.
- Mechanical components of cameras used in deep space.
- Astronaut space suite bearing and breathing apparatus lubricant.
- Robots in wafer handling in clean room environments.
- Scanning Electron Microscope (SEM) position table lubricant.
- Top coating lubricant on computer disc drive.
- Vacuum grease in semiconductor processing.
- Bearing in waste treatment facilities, & Anti-seize compounds.
- Automotive Breaking System (ABS).
- Impregnate for O-ring in pharmaceutical equipment.
- Pump seal and bearing lubricant in chlorine and strong oxidizer environments..

APPLYING PFPE

OIL FORM:

In closed and sealed applications, use oil for lubricating parts where a grease may be undesirable by means of the **Vacuum impregnating technique** as follow:

- Clean metal surface ultrasonically in a suitable solvent.
- Vacuum Bake @ minimum 29" Hg Vacuum and 120°F for 1 hour.
- Break vacuum to admit oil., Immerse bearing and O-ring.
- Vacuum bake again till bubbling ceases, release vacuum, remain 4 hours.
- Atmospheric pressure forces the impregnated oil into the bearing retainer.
- Remove parts from oil, drain, and centrifuge.

Impregnated part can weep oil over a long period of time in application

GREASE FORM:

In closed sealed/not sealed and in open bearing applications. In case there is not enough clearance to apply regular lubricant, OR concern about lubricant contamination for food industry use **Grease plating technique**, to apply thin uniform film of lubricant as follow:

- Grease + Volatile solvent (1:1) or other ratio, dip metal in mixture.
- Drain excess , heat to drive off solvent. Plate solution is stable for 6 hours
- By changing the ratio (1:1) we can control film thickness.

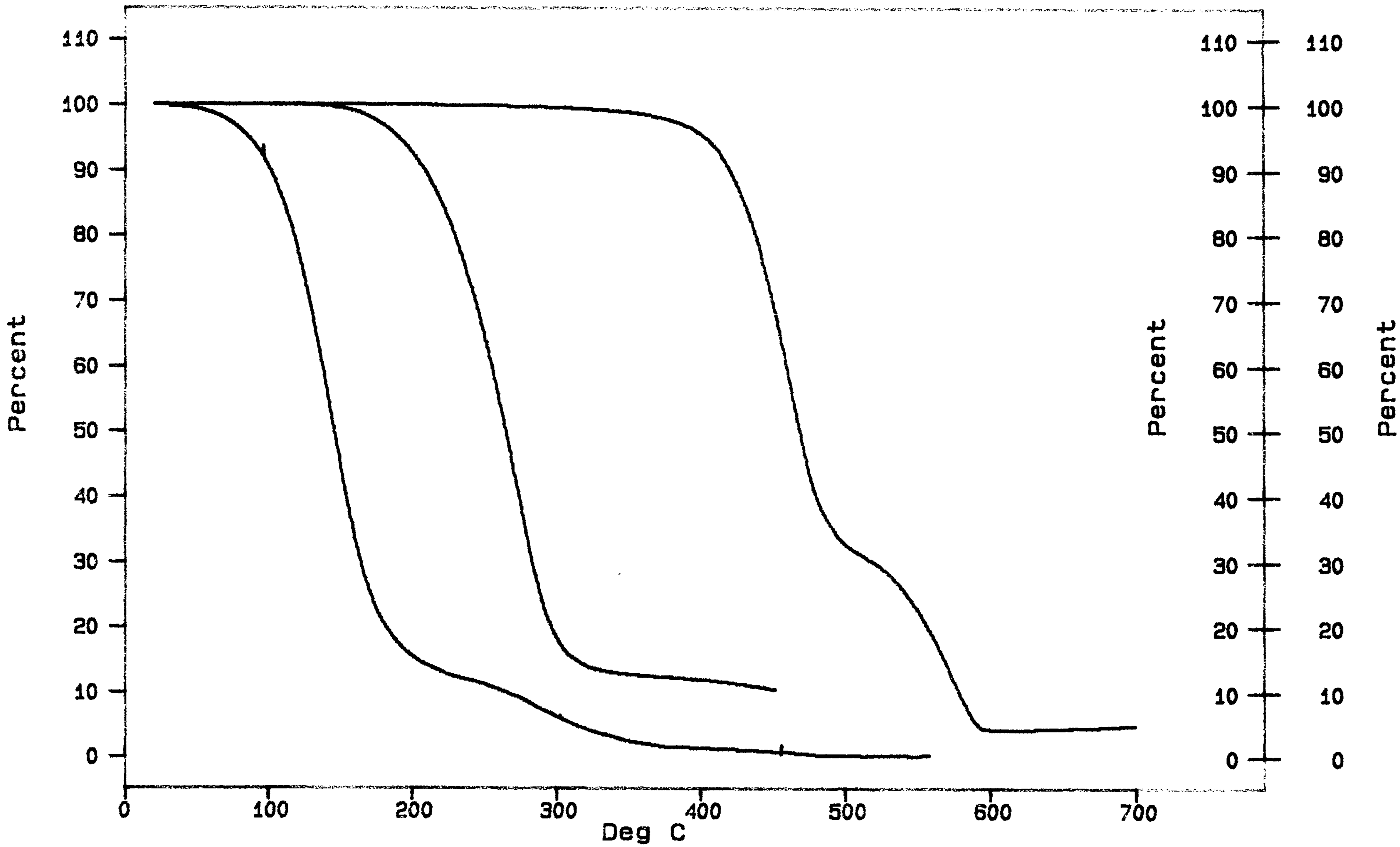
CLEANING PFPE:

Only fluorinated solvents can clean PFPE oils and greases. Hydocarbon solvents are not miscible with PFPE oils, so they can not clean it. Also PFPE oils has a very low surface tension than any hydrocarbon solvent, i.e., PFPE oil adheres strongly to the lubricated surface. More environmentally friendly solvents have been tested as replacements for Freon® 113. These solvents are short cabon chains, starting from five carbons saturated with fluorine atoms.

TGA 1000
PL Thermal Sciences

SMPL ID : BXL 258A
SMPL ID : GXL-297A, Mod.3
SMPL ID : BR783

COMMENT : 5A-7835
COMMENT : BMS3-33 Grease
COMMENT : WE26



VERSION: V4.30

MANUFACTURING OF PFPE:

- Polymerization reaction starting with homomonomers, undergoes photooxidation, followed by a reduction reaction to yield a bi-functional chain. This can be followed by special thermal treatment to yield a mono-functional chain.
- Photochemical fluorination, then distillation to produce the straight chain. Or vacuum crack, then thermal fluorination and distillation to produce branched chain.

ADDITIVE COMPATIBILITY: PFPE oils and greases may contain additives to enhance their temperature/viscosity characteristics, extreme pressure properties, oxidation resistance, corrosion inhibition, and wear resistance. It is important to consider the effect of these additives in the clean room environment, i.e., molybdenum disulfide, a common extreme pressure additive, can create particles when used in a dry film polluting the air.

EXPERIMENT ON PFPE AND Li-COMPLEX GREASES

1) Low Temp. Torque per ASTM D-1478 @ -100°F	PFPE	Li-Complex
Starting Torque	0.13 Nm	0.70 Nm
Running Torque 1hr	0.048 Nm	0.10 Nm

2) Oil Separation Test per FED-STD-791, Method 321	200hr at 400°F	24hr at 400°F
Oil Separation, %	14.18	21.75
Oil Evaporation, %	0.77	9.32
Total Weight Loss, %	14.95	31 .07

3) Low Temp. Torque per ASTM D-1478 @-100°F ,	with remaining grease after 2	
Starting Torque	0.33 Nm	Frozen
Running Torque 1hr	0.064 Nm	Frozen

DISCUSSION:

Step 1: The PFPE grease gives a very good torque results at -100°F when compared to a Li-complex grease using PAO/Ester base oil.

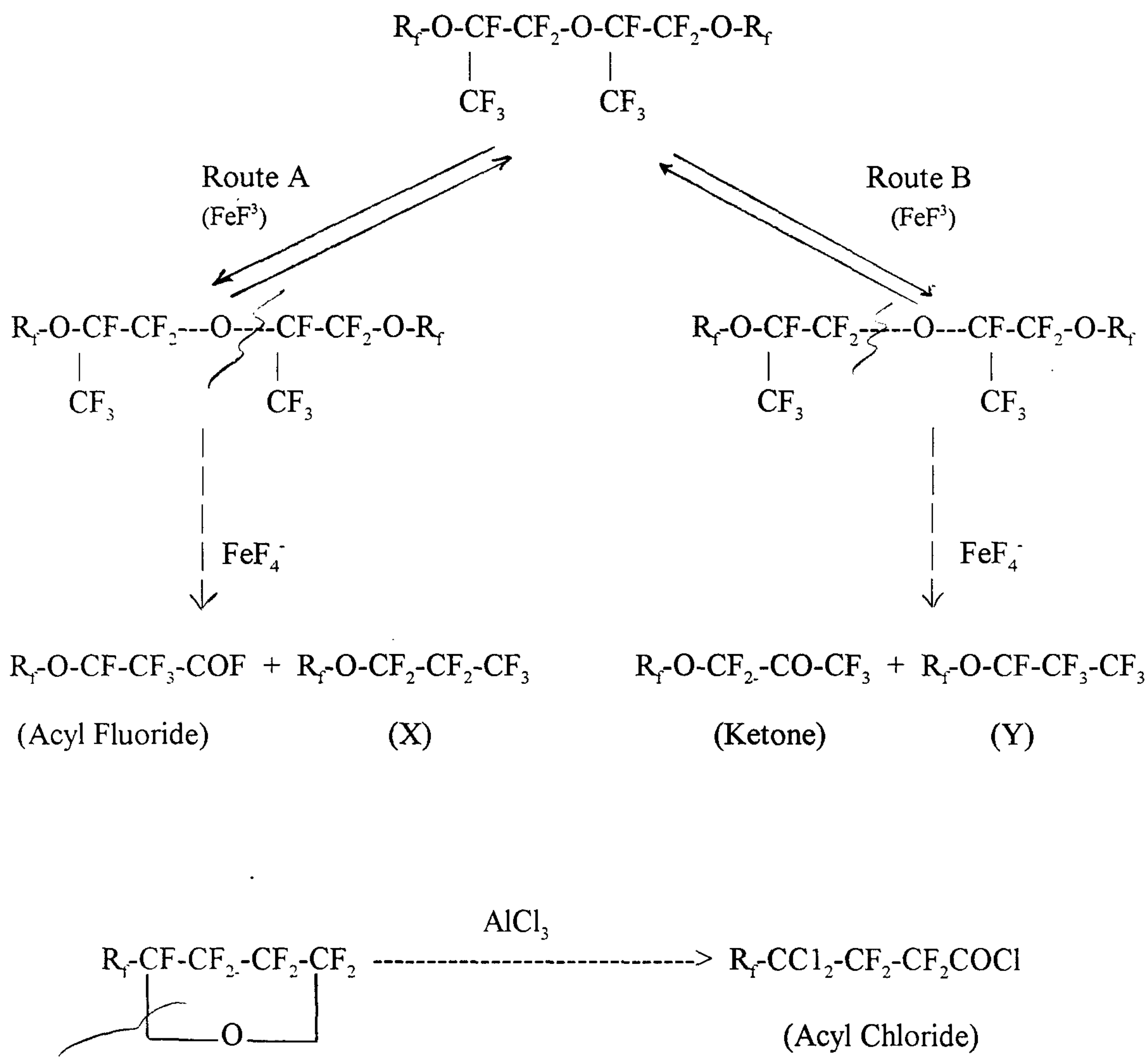
Step 2: The PFPE grease was tested for oil separation at 400°F for **200** hours and gave a better result than Li-Complex grease which was tested at 400°F for only **24** hours.

Step 3: The remaining PFPE grease from Step 2 gave almost the same result when tested for torque at -100°F, but the Li-Complex grease becomes frozen at -100°F.

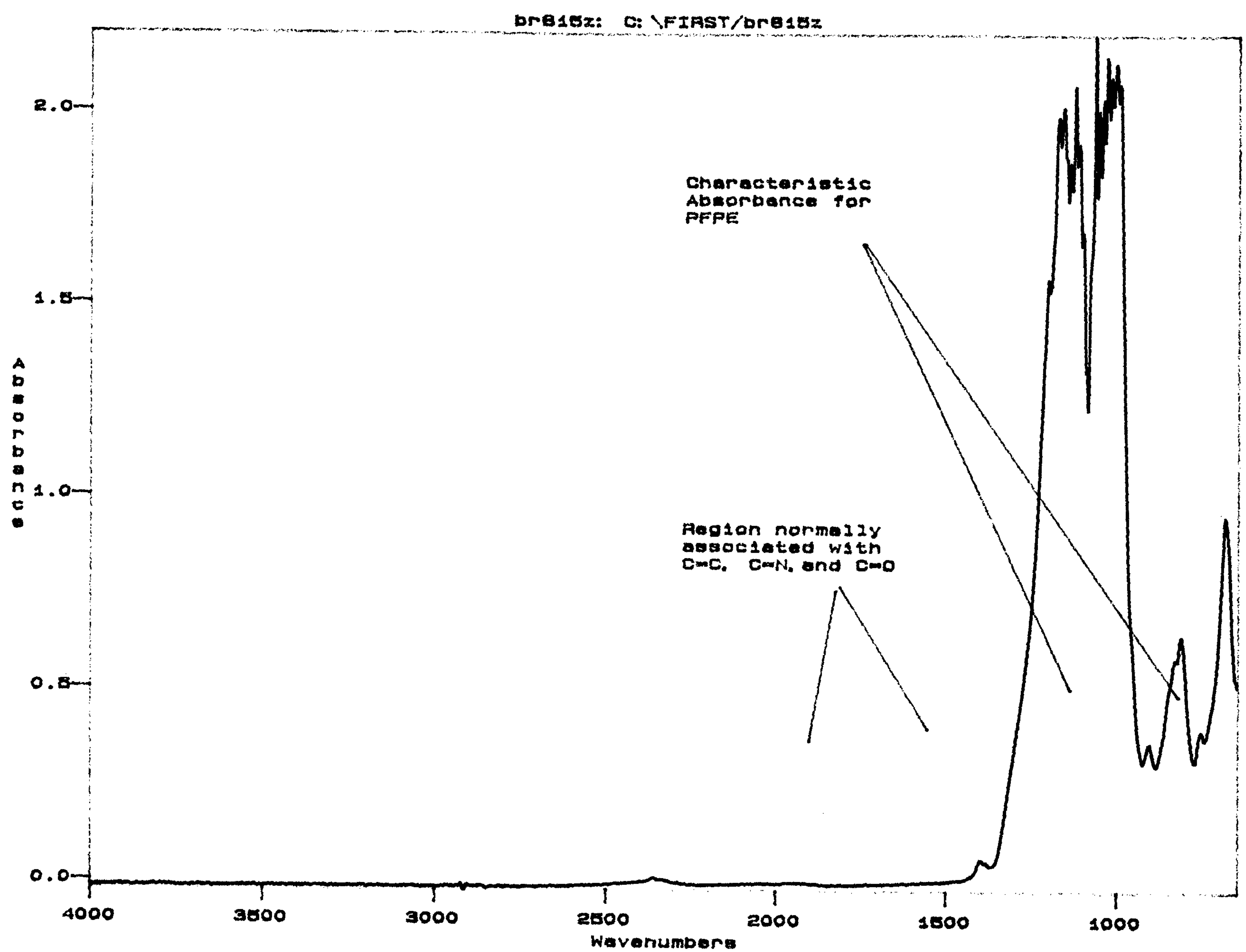
The above unique performance of PFPE is due to it's excellant low temperature property, high thermal stability, and low oil separation tendency.

DEGRADATION OF PFPE BY FeF_3 AND $AlCl_3$

R_f and R_f = Perfluoropolyalkylether end groups of unspecified length.



The reaction products acyl fluoride and ketone are those expected for the catalyst-assisted cleavage of the etherate carbon-oxygen bond.


br815z: C:\FIRST/br815z
Absorbance
2.0
1.5
1.0
0.5
0.0
4000
3500
3000
2500
2000
1500
1000
Wavenumbers
Characteristic
Absorbance for
PFPE
Region normally
associated with
C=C, C=N, and C=O

NEW GENERATION HIGH PERFORMANCE GREASE (HYBRID)

Fluorinated greases are very high in performance which is required by some specific applications where the high price of PFPE can be justified. For other less severe applications PFPE lubricants are very expensive. There was a need for a lubricating grease at an affordable cost to fill the gap between the fluorinated and non-fluorinated greases.

Another reason for developing hybrid grease was its ability to emulsify water, unlike PFPE alone. In some applications, where the grease is exposed to water, then exposed to a cold environment, the water present with the grease becomes ice leading to an increase in the bearing torque. An example of the above condition is the wheel bearing of an airplane. Hybrid greases can contain the ice droplets within it's structure giving a torque result lower than PFPE alone in similar conditions.

Also in hybrid greases we can add non-fluorinated additives which will enhance the grease performance in certain areas. PFPE oils and greases are limited to the use of fluorinated additives due to miscibility/compatibility issue.

A new family of cost-effective greases combining fluorinated products with mineral or synthetic oils have been developed. These greases show long operating life at a temperature range from -50°C to 190°C. Above or below this temperature range, only fluorinated lubricants can be used.

Generally speaking, the major reason for non-fluorinated grease failure is the increased consistency due to oil loss which occurs due to oil evaporation, degradation and migration In hybrid greases, rate of oil loss due to evaporation and degradation may be reduced by the formation of fluorinated film which reduces friction. The migration rate could also be reduced by the formation of a lower surface energy fluorinated film.

Several lab developed samples are being tested in the lab and in the field to fully define the performance characteristics of these new hybrid greases. The ratio of the PFPE grease to the non-PFPE in these hybrid greases can vary depending on the desired grease properties and cost limitations. Also the chemical composition of hybrid grease can vary by choosing from a wide variety of PFPE greases and mixing it with different types of soap-thickened greases to meet the application requirements.

Suggested applications for the hybrid greases will include:
Automotive electric fans and clutches, steel mills, drilling plants, paper production, thermo insulating panel, electronics, wheel bearing of an airplane, and personal computer production.

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